Wave Algorithms:
Optimal Database Search and Catalysis[1]

Apoorva D. Patel

Centre for High Energy Physics and Supercomputer Education and Research Centre
Indian Institute of Science, Bangalore-560012, India

Abstract. Grover's database search algorithm, although discovered in the context of quantum computation, can be implemented using any physical system that allows superposition of states. A physical realization of this algorithm is described using coupled simple harmonic oscillators, which can be exactly solved in both classical and quantum domains. Classical wave algorithms are far more stable against decoherence compared to their quantum counterparts. In addition to providing convenient demonstration models, they may have a role in practical situations, such as catalysis.

COMPUTING WITH WAVES

Any physical system—with some initial state, some final state, and some interaction in between—is a candidate for processing information. One only needs to construct a suitable map between physical properties of the system and abstract mathematical variables. Most of the development in computer algorithms has been in the framework of "particle-like" discrete digital languages. It is known that "wave-like" analogue computation can also be carried out (e.g. using RLC circuits), but that has not been explored as intensively. The obvious reason is that discrete variables allow a degree of precision, by implementation of error correction procedures, that continuous variables cannot provide. In addition, computational complexity is believed to be the same for digital and analogue algorithms, so the choice between the two is left to considerations of hardware stability.

With the advent of quantum computation, several quantum algorithms have been discovered, which are superior to their counterparts based on Boolean logic. Naturally, with both "particle-like" and "wave-like" behaviour at their disposal, quantum algorithms cannot do any worse than their classical counterparts. It is routinely stated that the simple parallelism provided by superposition and interference of quantum states is the key ingredient for the superiority of quantum algorithms. Now both superposition and interference are generic features of wave dynamics, and it is worthwhile to investigate the advantages they bring to an algorithm by exploring implementations based on "wave-like" behaviour alone. Of course, the classical wave implementations will be less efficient than the fully quantum ones, but they are expected to be much more stable (in

---

[1] Invited talk at the conference "Quantum Computing: BackAction 2006", IIT Kanpur, India, March 2006.

particular, they have no entanglement and much weaker decoherence) and so may turn out to be useful in specific situations. With this motivation, I study in this work, Grover's database search algorithm [1]—a straightforward and yet versatile algorithm that allows a variety of physical realisations.

The Optimal Search Algorithm

Database search is an elementary computational task, whose efficiency is measured in terms of the number of queries one has to make to the database in order to find the desired item. In the conventional formulation of the problem, the query is a binary oracle (i.e. a Yes/No question). For an unsorted database of N items, using classical Boolean logic, one requires on the average $\langle Q \rangle = N$ binary queries to locate the desired item. The number of queries is reduced to $\langle Q \rangle = (N+1)/2$, if the search process has a memory so that an item rejected once is not picked up again for inspection.

Grover discovered a search algorithm that, using superposition of states, reduces the number of required queries to $Q = O(\sqrt{N})$ [1]. This algorithm starts with a superposition state, where each item has an equal probability to get picked, and evolves it to a target state where only the desired item can get picked. Following Dirac's notation, and using the index i to label the items, the starting and the target state satisfy

$$|\langle i|s \rangle|^2 = 1/N , \quad |\langle i|t \rangle|^2 = \delta_{it} .\tag{1}$$

The algorithm evolves $|s\rangle$ towards $|t\rangle$, by discrete rotations in the two-dimensional space formed by $|s\rangle$ and $|t\rangle$, using the two reflection operators,

$$U_t = 1 - 2|t\rangle\langle t| , \quad U_s = 1 - 2|s\rangle\langle s| ,\tag{2}$$

$$(-U_s U_t)^Q |s\rangle = |t\rangle .\tag{3}$$

U_t is the binary oracle which flips the sign of the target state amplitude, while $-U_s$ performs the reflection-in-the-mean operation. Solution to Eq.(3) determines the number of queries as

$$(2Q+1)\sin^{-1}(1/\sqrt{N}) = \pi/2 .\tag{4}$$

(In practice, Q must be an integer, while Eq.(4) may not have an integer solution. In such cases, the algorithm is stopped when the state has evolved sufficiently close to, although not exactly equal to, $|t\rangle$. Then one finds the desired item with a high probability.)

In the qubit implementation of the algorithm, one chooses $N = 2^n$ and the items in the database are labeled with binary digits. With the uniform superposition as the starting state,

$$\langle i|s \rangle = 1/\sqrt{N} , \quad U_s = H^{\otimes n}(1 - 2|0\rangle\langle 0|)H^{\otimes n} ,\tag{5}$$

(H is the Hadamard operator), the implementation requires only $O(\log_2 N)$ spatial resources [1]. It has been proved that this is the optimal algorithm for unsorted database search [2].

Different physical realizations of the database items (e.g. binary labels or individual modes) and the target query oracle (e.g discrete binary operation or continuous time evolution) produce a variety of implementations of this algorithm. In the original version,

the states are encoded in an n-qubit register, and the oracle is a discrete binary operation (denoted by U_t above). In the analogue version of the algorithm, the discrete unitary oracle is traded for a continuous time interaction Hamiltonian, which evolves the target state somewhat differently than the rest and acts for the entire duration of the algorithm, and the number of queries is replaced by the time one has to wait for before finding the target state [3]. The wave version of the algorithm requires N distinct wave modes, instead of n qubits, but does not involve quantum entanglement at any stage [4]. Such a wave search has been experimentally implemented using classical Fourier optics, with a phase-shift plate providing the oracle [5]. An analogue version of the algorithm has been described using a classical coupled pendulum model, where one of the pendulums is slightly different than the rest and the uniform superposition state $|s\rangle$ is identified with the center-of-mass mode [6]. In what follows, I describe a binary oracle version of the wave search algorithm using identical coupled harmonic oscillators.

HARMONIC OSCILLATOR IMPLEMENTATION

A harmonic oscillator is the favourite model of physicists. It provides the first approximation in a wide variety of physical phenomena involving small fluctuations about an equilibrium configuration. Its mathematical description contains only quadratic forms, in position as well as momentum coordinates. It can be solved exactly in both classical and quantum domains, which makes it extremely useful in situations where a cross-over between classical and quantum behaviour is to be analyzed. We shall first look at the classical system, and then observe that the quantum system essentially follows the same pattern.

Classical Oscillators

Let the items in the database be represented by N identical harmonic oscillators. While they are oscillating in a specific manner, someone taps one of the oscillators (i.e. elastically reflects it by touching it). The task is to identify which of the oscillators has been tapped, without looking at the tapping—quite like a magician who can tell which one of his cards was touched when he was blindfolded. The optimization criterion is to design the system of oscillators, and their initial state, so as to make the identification as quickly as possible.

Grover's algorithm requires identical coupling between any pair of oscillators. This can be accomplished by coupling all the oscillators to a big oscillator, as shown in Fig.1. The big oscillator is thus coupled to the centre-of-mass mode, and becomes an intermediary between any pair of oscillators with the same strength. The Lagrangian for the whole system is

$$\mathcal{L} = \frac{1}{2}M\dot{X}^2 - \frac{1}{2}KX^2 + \sum_{i=1}^{N}[\frac{1}{2}m\dot{x}_i^2 - \frac{1}{2}k(x_i - X)^2] \ . \tag{6}$$

With the center-of-mass displacement, $\bar{x} \equiv \sum_{i=1}^{N} x_i/N$, the Lagrangian can be rewritten as

$$\mathcal{L} = \frac{1}{2}M\dot{X}^2 - \frac{1}{2}KX^2 + \frac{1}{2}Nm\dot{\bar{x}}^2 - \frac{1}{2}Nk(\bar{x}-X)^2 + \sum_{i=1}^{N}[\frac{1}{2}m(\dot{x}_i - \dot{\bar{x}})^2 - \frac{1}{2}k(x_i - \bar{x})^2] . \quad (7)$$

Now we can fix the oscillator parameters to implement Grover's algorithm. In the algorithm, we are interested in the dynamics of the tapped oscillator. All the other oscillators (i.e. $i \neq t$) influence the dynamics of x_t only through the combination $\bar{x}$. The dynamics of $(N-2)$ linearly independent modes orthogonal to x_t and $\bar{x}$ (they all have the form $(x_{j \neq t} - x_{k \neq t})$) decouples from the modes of interest; we can drop them and effectively work in the 3-dimensional space of the modes $\{X, \bar{x}, x_t\}$. (In what follows, I shall first specify initial conditions such that all $x_{i \neq t}$ are identical and all the decoupled modes vanish. Subsequently, we will look at the general situation by adding back all the decoupled modes.)

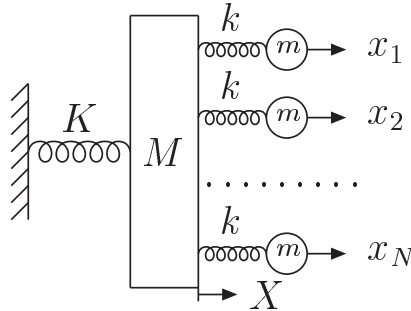Choosing units of mass and time such that $m = 1, k = 1$, and in terms of the variables

$$Y = \sqrt{M}X , \quad \bar{y} = \sqrt{N}\bar{x} , \quad y_t = x_t - \bar{x} , \quad (8)$$

the effective Lagrangian becomes

$$\mathcal{L}_{\text{eff}} = \frac{1}{2}\dot{Y}^2 - \frac{1}{2}\frac{K}{M}Y^2 + \frac{1}{2}\dot{\bar{y}}^2 - \frac{1}{2}\left(\bar{y} - \sqrt{\frac{N}{M}}Y\right)^2 + \frac{N}{2(N-1)}\dot{y}_t^2 - \frac{N}{2(N-1)}y_t^2 . \quad (9)$$

The potential energy terms in $\mathcal{L}_{\text{eff}}$ are easily diagonalized, and yield the eigenvalues

$$\omega_{\pm}^2 = \frac{1}{2}\left(1 + \frac{K+N}{M}\right) \pm \sqrt{\frac{1}{4}\left(1 + \frac{K+N}{M}\right)^2 - \frac{K}{M}} ,$$

$$\omega_+^2 + \omega_-^2 = 1 + \frac{K+N}{M} , \quad \omega_+^2\omega_-^2 = \frac{K}{M} , \quad \omega_t = 1 . \quad (10)$$

FIGURE 1. A system of N identical harmonic oscillators, coupled to a big oscillator via the center-of-mass mode.

The corresponding eigenmodes are

$$e_{\pm} = (1 - \omega_{\pm}^2)Y + \sqrt{\frac{N}{M}}\bar{y} = (1 - \omega_{\pm}^2)\sqrt{M}X + \frac{N}{\sqrt{M}}\bar{x} , \tag{11}$$

$$e_t = y_t = x_t - \bar{x} .$$

The initial uniform superposition state can be realized as all the oscillators moving together, while the big oscillator is at rest.

$$t = 0: \quad X = 0 , \ \dot{X} = 0 , \ x_i = 0 , \ \dot{x}_i = A . \tag{12}$$

(We will consider situations with general initial conditions later.) The reflection operators correspond to shifting the appropriate oscillator phases by half a period. The binary tapping oracle can be realized as the elastic reflection illustrated in Fig.2. That implements U_t in the velocity space, by reversing the target oscillator velocity at the instance when all the displacements vanish. Time evolution of the coupled oscillators redistributes the total kinetic energy, and that can implement the operator U_s with a suitable choice of time interval and frequencies.
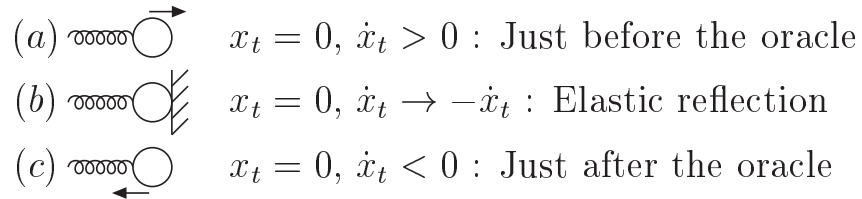
With the natural frequency of individual oscillators $\omega = \sqrt{k/m} = 1$, the reflection-in-the-mean operation requires $\omega_{\pm}$ to be rational numbers. Optimization means that they should be selected to make the dynamics of the whole system of oscillators have as small a period as possible. The solution is not unique. One set of solutions is (p is a positive integer)

$$\omega_+ = \frac{2p+1}{2} , \ \omega_- = \frac{1}{2} \implies M = \frac{16Nm}{3(2p+3)(2p-1)} , \ K = \frac{(2p+1)^2 Nk}{3(2p+3)(2p-1)} . \tag{13}$$

In these cases, in absence of oracles, the dynamics of the whole system of oscillators has the period, $T = 4\pi$. The big oscillator returns to its initial rest state ($X = 0, \dot{X} = 0$), whenever t is an integral multiple of 2π, i.e. after every half a period. Time evolution for the same interval of half a period reverses $\dot{\bar{x}}$, while leaving $\dot{x}_t - \dot{\bar{x}}$ unchanged, i.e. it implements the operator U_s in the velocity space. Thus Grover's algorithm, Eq.(3), can be realized by applying the tapping oracle at every time interval $\Delta t = 2\pi$.

A more interesting set of solutions is

$$\omega_+ = 2p , \ \omega_- = 0 \implies M = \frac{Nm}{(2p+1)(2p-1)} , \ K = 0 . \tag{14}$$

(a) ⟀⟀◯ $\quad x_t = 0, \dot{x}_t > 0 :$ Just before the oracle

(b) ⟀⟀◯ $\quad x_t = 0, \dot{x}_t \to -\dot{x}_t :$ Elastic reflection

(c) ⟀⟀◯ $\quad x_t = 0, \dot{x}_t < 0 :$ Just after the oracle

FIGURE 2. The binary tapping oracle flips the sign of the target oscillator velocity, when its displacement is zero.

Under these conditions, the big oscillator is not coupled to any support, and e_- becomes a translation mode for the whole system of oscillators. The translation mode can be eliminated from the dynamics with the initial conditions

$$t = 0: \quad X = 0 \,, \ \dot{X} = -\frac{N}{M}A \,, \ x_i = 0 \,, \ \dot{x}_i = A \,. \tag{15}$$

Then, in absence of oracles, the dynamics of the whole system of oscillators has the smallest possible period, $T = 2\pi$. After half a period, the big oscillator is back to its initial state, $\dot{\bar{x}}$ also returns to its initial value, while $\dot{x}_t - \dot{\bar{x}}$ changes its sign. This is equivalent to applying $-U_s$ in the velocity space, and Grover's algorithm can be implemented by tapping the target oscillator at every time interval $\Delta t = \pi$.

There is an important physical distinction between the quantum and the wave implementations of the amplitude amplification process in Grover's algorithm—quantum probability is mapped to wave energy. The enhancement of the quantum amplitude increases the probability of finding the target state N-fold, while the enhancement of the wave amplitude increases the energy of the target oscillator N-fold. The well-known phenomenon of "beats" is responsible for energy transfer amongst coupled oscillators. The elastic reflection oracle does not change energy, and it is interesting to observe that the oscillator which is obstructed by tapping picks up energy.

Stability Considerations

Now we can look at the behaviour of the wave implementation under more general circumstances. First consider the initial conditions. Despite appearances, precise synchronization of oscillators is not an issue in the algorithm, because of the explicit coupling to the center-of-mass mode. For instance, the algorithm can be started off with an initial push to the big oscillator, $\dot{X} = B, \dot{x}_i = 0$, and the system of oscillators would evolve to the stage $\dot{X} = 0, \dot{x}_i = A$. Furthermore, any arbitrary distribution of initial velocities of oscillators can be accommodated in the analysis by bringing back the $(N-2)$ decoupled modes. The decoupled modes have no effect whatsoever on the dynamics of the $\{X, \bar{x}, x_t\}$ modes. Consequently, they modify the algorithm only to the extent that the energy amplification of the target oscillator is limited to the initial energy present in the $\{X, \bar{x}, x_t\}$ modes, instead of being N-fold. Explicitly, the maximum gain is

$$\left[\left(N\dot{\bar{x}}^2 + \frac{N}{(N-1)}(\dot{x}_t - \dot{\bar{x}})^2 \right) \Big/ \dot{x}_t^2 \right]_{t=0} \,, \tag{16}$$

which can be substantial for the generic situation where the initial $\dot{x}_t$ and $\dot{\bar{x}}$ are of the same order of magnitude.

To extract the maximum gain, the algorithm must be stopped at a precise instant (i.e after a precise number of tapping oracles Q); otherwise the evolution continues in repetitive cycles. The state evolution in Grover's algorithm is a rotation at a uniform rate in the two dimensional $|s\rangle$-$|t\rangle$ subspace. The average overlap of the target state, with the state $|q(Q)\rangle$ after Q queries, is therefore

$$|\langle q(Q)|t\rangle|_{\text{av}}^2 = \langle \sin^2 \theta \rangle_{\text{av}} = 1/2 \,. \tag{17}$$

Thus if the algorithm is stopped at a random instant, the energy gain on the average is half of its maximum value in Eq.(16)—which can still be substantially larger than 1.

Next consider the effect of damping. Damping for a harmonic oscillator has to be analyzed using its equation of motion; it cannot be described using a time-independent Lagrangian. The standard description is:

$$\ddot{x} + 2\gamma\dot{x} + \omega_0^2 x = 0 \implies x = Ae^{-\gamma t}\cos\left(\sqrt{\omega_0^2 - \gamma^2}\, t + \phi\right) . \tag{18}$$

The crucial ingredient in the algorithm is the coherence amongst the phases of the oscillators. That is governed by the frequencies of the oscillators, and is independent of the amplitudes. For a weakly damped oscillator, its amplitude changes linearly with the damping coefficient, while its frequency changes quadratically. The time evolution of the above implementation, therefore, remains essentially unaffected if the oscillators experience a small damping. The dominant effect is a decrease in the energy amplification due to decaying amplitudes.

Among other variations, simultaneous scaling of masses and spring constants of the oscillators (i.e. $m_i = \alpha_i m$ and $k_i = \alpha_i k$) does not alter the algorithm at all, since the scale factors can be absorbed by redefining x_i. One can also contemplate interchange of the initial and the final states, since the algorithm is fully reversible. The evolution would then run backwards, and the physical interpretation would be the dissipation of a large initial energy of the target oscillator in to a uniform distribution over all the coupled oscillators.

Quantum Domain

The dynamics of harmonic oscillators is simple enough to permit exact quantum analysis as well. It is convenient to interpolate between classical and quantum domains using the coherent state formulation (see for example, Ref. [7]). Coherent states are superpositions of the energy eigenstates, parametrized by a single complex variable α,
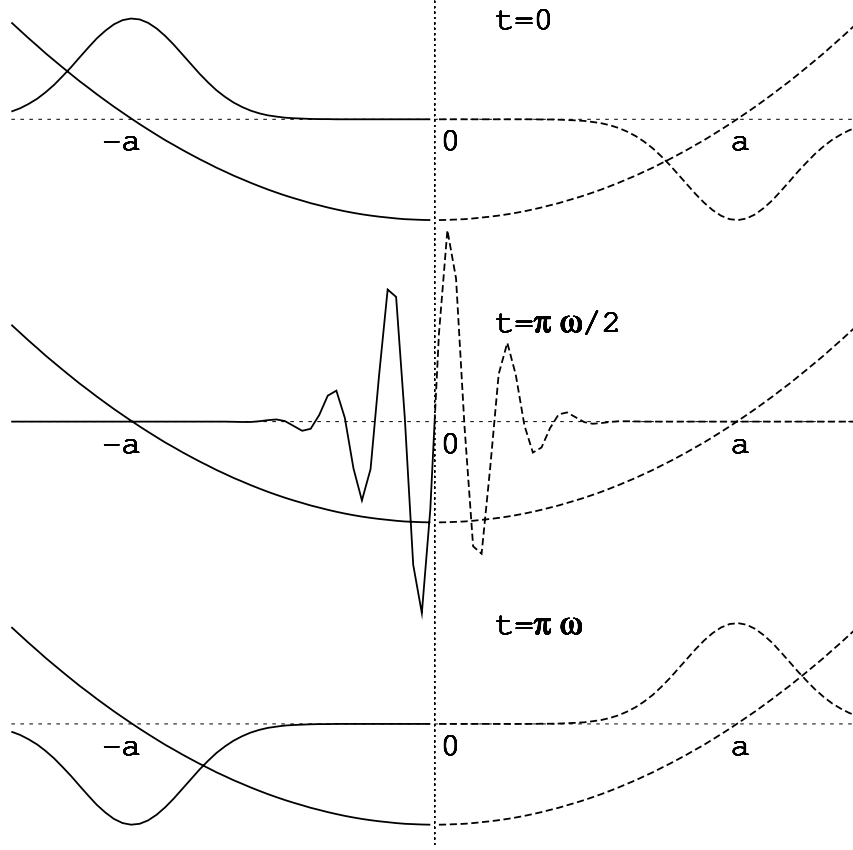
$$|\alpha\rangle = e^{-|\alpha|^2/2}\sum_n \frac{\alpha^n}{\sqrt{n!}}\, |n\rangle . \tag{19}$$

They describe Gaussian wavepackets with minimal spread (i.e. displaced versions of the ground state eigenfunction),

$$\Delta x = \sqrt{\frac{\hbar}{2m\omega}}, \quad \Delta p = \sqrt{\frac{m\hbar\omega}{2}} . \tag{20}$$

A coherent state with the initial condition $\alpha(t=0) = \alpha_0$ has energy $\hbar\omega(|\alpha_0|^2 + \frac{1}{2})$, and the centre of its wavepacket performs the same simple harmonic motion as a classical particle would,

$$\alpha_0 e^{-i\omega t} = \frac{\langle x\rangle(t)}{2\Delta x} + i\frac{\langle p\rangle(t)}{2\Delta p} . \tag{21}$$

FIGURE 3. Evolution of the coherent state wavefunction of the tapped oscillator, with the initial condition $\alpha_0 = -a$, The left half of the figure shows the actual wavepacket in the half-harmonic oscillator potential, with the impenetrable wall at $x = 0$. The right half of the figure shows the image wavepacket that ensures the node of the wavefunction at $x = 0$. For $t = \pi\omega/2$, the wavefunction is purely imaginary, but the factor of i is omitted for convenience in drawing the figure. The wavepacket at $t = \pi\omega$ includes the geometric phase of -1 arising from reflection.

The wavefunction of the state evolves according to

$$|\psi(0)\rangle = |\alpha_0\rangle \implies |\psi(t)\rangle = e^{-i\omega t/2}|\alpha_0 e^{-i\omega t}\rangle \,, \tag{22}$$

while the explicit structure of the wavepacket is given by

$$\psi(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left[-\left(\frac{x - \langle x\rangle}{2\Delta x}\right)^2 + i\frac{x\langle p\rangle}{\hbar}\right] . \tag{23}$$

Thus the classical analysis of previous sections can be carried over unchanged to the quantum domain, provided we can figure out how the tapping oracle works for the coherent states. The tapped oscillator corresponds to a particle moving in the half-

harmonic oscillator potential

$$V(x) = \tfrac{1}{2}kx^2 \ \text{ for } x \leq 0 \ , \ \ V(x) = \infty \ \text{ for } x > 0 \ . \tag{24}$$

The impenetrable wall at $x = 0$ is equivalent to enforcing the boundary condition $\psi(x = 0) = 0$. So the energy eigenstates of the half-harmonic oscillator are the same as those for the harmonic oscillator, with odd n. It is straightforward to ensure the node at $x = 0$ using the method of images, and the tapped oscillator coherent states become

$$|\alpha_t\rangle = C\big(|\alpha\rangle - |-\alpha\rangle\big) \ , \tag{25}$$

with a time-independent normalization constant $C = (1 - e^{-2|\alpha|^2})^{-1/2}$. Tapping amounts to change-over between $|\alpha\rangle$ and $|-\alpha\rangle$, which reverses $\langle x \rangle$ and $\langle p \rangle$ compared to the untapped motion. In addition, the wavefunction changes sign, which is the geometric phase corresponding to wave reflection. The evolution of a coherent state wavepacket undergoing a reflection from the wall is depicted in Fig.3.

POSSIBLE APPLICATIONS

The oscillator based search process discussed above has the same algorithmic efficiency as the proposals of Refs.[6, 5, 4]—where it differs from them is in the actual physical implementation. All these wave implementations require exponentially more spatial resources compared to their digital counterparts, $O(N)$ vs. $O(\log_2 N)$. On the other hand, they reduce the number of oracle calls by exploiting superposition of states. Note that no algorithm based on Boolean logic, either with serial or with parallel implementation, can reduce the number of oracle calls for an unsorted database search to less than $O(N)$.

Quantum algorithms are superior to wave algorithms, because they can use superposition as well as reduce spatial resources. The reduction of spatial resources, however, comes with the cost that quantum algorithms have to work with entangled states. Quantum entanglement is far more sensitive to decoherence caused by environmental disturbances than mere superposition, and that has made physical implementations of quantum algorithms very difficult. On the other hand, superposition of classical waves can be fairly stable, even in presence of a small amount of damping, and that can make wave implementations advantageous in specific physical contexts.

These features indicate that wave algorithms fall in a regime in between classical and quantum algorithms—more efficient than the former and more robust than the latter. They are likely to be useful in practical situations, where N is not very large and environmental disturbances are not negligible. Indeed it is worthwhile to systematically explore them, just like randomized algorithms have been [8].

In the specific case of the unsorted database search problem, the remarkable simplicity of the oscillator implementation would allow construction of convenient demonstration models, which can demonstrate the power of quantum algorithms even at school level. Going further, the practically useful property of the wave search algorithm is that it focuses energy of many oscillator modes into one of them. So it is really interesting to think of situations where the energy amplification process can have dramatic consequences. One such possibility is very familiar to all of us—the Boltzmann factor where the energy

is in the exponent—and I describe below a scenario for catalysis where involvement of new mechanisms can enhance our understanding of the observed phenomena.

Catalysis

There exist a large number of chemical reactions which, although not forbidden by energy conservation, are extremely slow because they have to pass through an intermediate state of high energy. In these reactions, the dominant term governing the reaction rate is the Boltzmann factor, $\exp(-E_b/kT)$, with the barrier energy in the exponent. Only a tiny fraction of the molecules in the tail of the thermal distribution are energetic enough to go over the barrier and complete the reaction. It is known that the rates of many such reactions can be enhanced by orders of magnitude by adding suitable catalysts (enzymes in case of biochemical reactions) to the reactants. The conventional explanation for the reaction rate enhancement, called transition state theory, is that the catalysts lower the energy of the intervening barrier by altering the chemical environment of the reactants.

The preceding analysis of the wave search algorithm suggests another mechanism for catalysis. Vibrations and rotations of molecules are ubiquitous harmonic oscillator modes. The catalyst can act as the big oscillator and transfer energy of many modes to the reactant which faces the energy barrier. For example, the catalytic substrate can have many identical molecules of one reactant stuck to it and vibrating, the second reactant then comes drifting along and interacts with one of the stuck molecules, that molecule picks up energy from its neighbours and the reaction gets completed. The rate enhancement results not from lowering of the energy barrier but from increase of the reactant energy. In such a scenario, for maximum efficiency, the physical parameters (masses and spring constants) need to have specific values. But even without perfectly tuned parameters, there can be partial energy focusing that provides useful increase in the reaction rate. Whether this mechanism exists among the known catalysts, or whether we can design new type of catalysts that use this mechanism, is open to investigation.

The contributions of the "transition state" and the "energy transfer" mechanisms to a catalytic effect are not mutually exclusive. So it is desirable to identify characteristics that can tell one of them apart from another. I point out two observable features that can distinguish the role of chemical environment from physical waves:

(1) Isotopic substitution in the reactants changes physical parameters without altering chemical properties. The electronic potential is essentially independent of the nuclear mass, and mass dependence enters the conventional transition state theory only through diffusion and tunneling effects. This mass dependence is rather weak and monotonic. On the other hand, the nuclear mass strongly affects vibration and rotation frequencies, which can substantially alter the energy transfer amongst coupled oscillator modes. Also, resonant energy transfer is not monotonic, i.e. it decreases on either side of the optimal parameter value.

(2) In the transition state theory, the reaction takes place between individual reactant molecules. On the other hand, energy transfer is a cooperative phenomenon that cannot occur without participation of nearby oscillator modes or molecules with similar properties. It would therefore be enhanced by existence of non-reacting but similar chemical

bonds close to the reaction site, and also by increasing concentration of the reactants.

Kinetic Isotope Effect

In the context described above, isotope dependence of reaction rates is a signal of involvement of physical (in contrast to chemical) features in the catalytic process. Many examples of isotopic dependence of catalytic reaction rates have been discovered, and the effect is referred to as the "Westheimer effect" or the "kinetic isotope effect" [9]. The effect is the largest for substitution of hydrogen by deuterium or tritium, and has been extensively studied for the rupture of C-H/C-D/C-T bonds. The conventional transition state theory has been found inadequate for a theoretical understanding in several cases involving enzymes, and vibrationally enhanced quantum tunneling has been invoked as an alternative [10].

Specifically, the observed kinetic isotope effects are divided in to two categories. The "primary effect" results from isotopic substitution of the hydrogen atom that is exchanged between the reactants. The "secondary effect" arises from isotopic substitution of a hydrogen atom that is not exchanged during the reaction but is adjacent to the exchanged one. Empirical models of reaction coordinate transition have been constructed, but they require effects of quantum tunneling under the barrier as well as contribution from vibrational bond energy to explain the size of the observed effects. In particular, the secondary effect cannot be explained at all without invoking coupled dynamics of atoms [11]. All these additional contributions enhance the reaction rates beyond their values in the classical transition state theory, and hence would be favoured in useful biochemical processes by natural selection during evolution. The observed results, however, are quoted as ratios of reaction rates to eliminate unknown normalization constants.

Against this backdrop, the coupled oscillator based energy transfer mechanism described in earlier sections offers several novelties:

(i) The whole analysis is based on first principles. For N coupled oscillators, just a single reflection can amplify the vibrational energy by a factor of $(3 - \frac{4}{N})^2$, which can be as large as 9. Of course, the maximum amplification possible (with more reflections) is N.

(ii) The vibrational modes contributing to catalysis must be soft, i.e. $\hbar\omega = O(kT)$, so that they can get thermally excited and participate in the dynamics. This will produce a characteristic temperature dependence, with the vibrational contribution dropping out at low enough temperatures.

(iii) Resonant energy transfer requires good frequency matching between coupled oscillator modes, as in Eqs.(13,14). Some of that can be inferred from the molecular structures (e.g. similar C-H bonds involved in secondary kinetic isotope effect), and more can be tested by spectroscopic methods.

(iv) The wavefunction sign-flip caused by reflection can switch between bonding and anti-bonding molecular orbitals (see Fig.4), and thus help in transfer of atoms. This feature is not related to either the mass or the temperature.

Clearly, the coupled oscillator inspired catalytic mechanism needs to be explored further, with careful modeling of specific reactions. It would be an impressive achievement indeed, if the detailed understanding can be used in design of new types of catalysts.
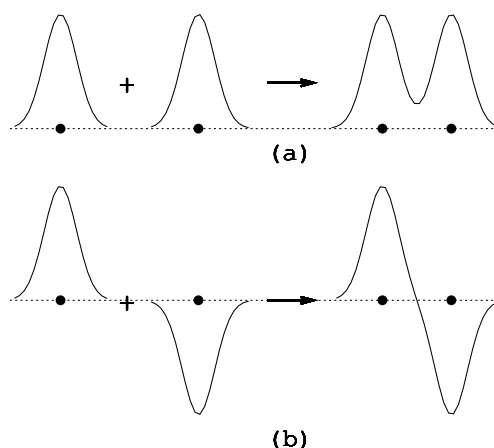
FIGURE 4. Formation of molecular bonds by overlap of electron clouds: (a) a binding orbital is formed when the two wavefunctions are in phase, (b) an anti-binding orbital results when the two wavefunctions have opposite phases.

ACKNOWLEDGMENTS

REFERENCES

1. L. K. Grover, "A Fast Quantum Mechanical Algorithm for Database Search," in Proceedings of the 28th Annual ACM Symposium on Theory of Computing (STOC'96), ACM Press, New York, 1996 pp. 212–219, e-print quant-ph/9605043.
2. C. Zalka, *Phys. Rev.* **A60**, 2746–2751 (1999), e-print quant-ph/9711070.
3. E. Farhi and S. Gutmann, *Phys. Rev.* **A57**, 2403–2406 (1998), e-print quant-ph/9612026.
4. S. Lloyd, *Phys. Rev.* **A61** 010301(R) (2000), e-print quant-ph/9903057.
5. N. Bhattacharya, H. B. van Linden van den Heuvell and R. J. C. Spreeuw, *Phys. Rev. Lett.* **88** 137901 (2002), e-print quant-ph/0110034.
6. L. K. Grover and A. M. Sengupta, *Phys. Rev.* **A65** 032319 (2002), e-print quant-ph/0109123.
7. C. Cohen-Tannoudji, B. Diu and C. Laloë, *Quantum Mechanics*, John Wiley and Sons, New York, 1977, Complement G_V.
8. R. Motwani and P. Raghavan, *Randomized Algorithms*, Cambridge University Press, Cambridge, 1995.
9. F. H. Westheimer, *Chem. Rev.* **61** 265–273 (1961).
10. W. J. Bruno and W. Bialek, *Biophys. J.* **63** 689–699 (1992);
    A. Kohen and J. P. Klinman, *Chem. Biol.* **6** R191–R198 (1999);
    M. J. Sutcliffe and N. S. Scrutton, *Phil. Trans. R. Soc. Lond.* **A358** 367–386 (2000);
    P. Ball, *Nature* **431** 396–397 (2004).
11. W. P. Huskey and R. L. Schowen, *J. Am. Chem. Soc.* **105** 5704–5706 (1983);
    D. Antoniou, S. Caratzoulas, C. Kalyanaraman, J. S. Mincer and S .D. Schwartz, *Eur. J. Biochem.* **269** 3103-3112 (2002);
    M. J. Knapp and J. P. Klinman, *Eur. J. Biochem.* **269** 3113-3121 (2002).
12. A. Patel, *Int. J. Quant. Inform.* **4** (2006), e-print quant-ph/0401154.